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CORROSION OF FIBER COMPOSITES WITH ALUMINUM ALLOY MATRIXES.(U)  
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1. In experimental Al-Mg composites with alumina fibers, preferential pitting at fibers and enhanced corrosion rates were observed and explanations given of their relation to segregation in the solidification structure. 2. Some of the corrosion of an Al-Li composite with alumina fibers are reported. 3. Studies of Al-Fe alloys with a cathodic phase showed the rate of pitting to be sensitive to microstructure and fine continuous structure to give rapidly accelerating corrosion. Equations for corrosion-time in continuous and discontinuous structures were derived in terms of quantitative

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metallography parameters with certain assumptions regarding pit nucleation and growth. In solutions yielding preferential dissolution of the cathodic phase, fine continuous structures are predicted to be superior. Discontinuous structures were superior from the viewpoint of corrosion in both cases.

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CORROSION OF COMPOSITES WITH ALUMINUM ALLOY MATRIXES

FINAL REPORT

M. Metzger

August 8, 1980

U.S. ARMY RESEARCH OFFICE

DAAG-29-77-G-0025  
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### STATEMENT OF THE PROBLEM

In recent years, substantial effort has gone into the development of aluminum-matrix fiber-reinforced composites, which are attractive for their potential as high strength/weight materials. Attention has been focussed on fiber materials, processing techniques and mechanical properties with little attention to corrosion behavior. Metal-matrix composites may be subject to corrosion problems associated with galvanic coupling, the presence of an interface bonding layer, microsegregation resulting from processing, or crevicing at a second phase. The present work sought to generate some systematic information on the corrosion of aluminum-matrix composites which would be available in support of development efforts. It was desirable that this work would include composites of the types under development. Composites with graphite fibers were originally considered, but it was found that material with the required control of metallurgical structure for the present purposes was not yet available and, after consultation with the sponsoring agency, work was undertaken with composites based on alumina fibers. In addition, Al-Fe eutectic composites were selected for study as a model system which could be prepared with varying spacing and continuity. Electrochemical measurements and microstructure characterization were performed employing several solutions appropriate for accelerated testing.

## RESEARCH RESULTS

### 1. Corrosion of Experimental Al-Mg/Al<sub>2</sub>O<sub>3</sub> Composites

Since composite processing techniques were under development at this institution by Professor R. Mehrabian's group, material prepared to our specifications was available through their cooperation. The composites studied had an Al-2% Mg matrix with low volume fractions of discontinuous DuPont FP Al<sub>2</sub>O<sub>3</sub> fibers and were prepared by Rheocasting, fiber alignment being obtained by extrusion. A set of materials was prepared with a relatively high purity alloy matrix consisting of the composite (C), the matrix alloy processed in the same way but without fibers and the matrix alloy unprocessed and conventionally cast. A previously prepared experimental composite (7C) with a matrix of commercial purity and processing conducive to more severe segregation was selected for comparison. Commercial sheet of 5052-H34 and 6061-T6 plus one lot of very high purity Al-1%Mg alloy known to have uniform distribution of Mg were included for reference. Studies were made in 53 g/L NaCl + 3 g/L H<sub>2</sub>O<sub>2</sub> of corrosion potential, cathode polarization, and galvanostatic anode polarization. Anode polarization below the pitting potential was studied in deaerated solutions without H<sub>2</sub>O<sub>2</sub>. To permit study of pit distribution, exposures were designed for light corrosion, thus with little weight loss, and corrosion rates were deduced qualitatively from the cathode polarization data. To deal with the question of preferential pitting near fibers, the general concept of "anodic sites", at which film breakdown and pitting initiate preferentially, was developed through analysis of transient and stable pitting in the various materials studied.

The results showed these composites to be subject to some preferential pitting near fibers, which was severe in 7C, and they had higher than expected corrosion rates. From SEM pit morphology and microprobe observations, preferential pit nucleation near fibers was attributed to a segregation of Mg which was incompletely dispersed in extrusion and annealing and which was sufficient to give in certain locations precipitation of the anodic Mg<sub>5</sub>Al<sub>8</sub> phase. Preferential growth of stable pits near fibers was also noted and was attributed to the enhanced Mg content of the local solid solution and the consequent lowering of the pitting potential. The thin MgAl<sub>2</sub>O<sub>4</sub> interface phase in this composite did not influence corrosion. The tendency to enhanced corrosion rates was attributed to Fe segregation near fibers and the exposure by the preferential pitting there of Fe-bearing cathodic phases. In contrast, the commercial 5052 alloy for example showed less corrosion despite its higher Fe content because the Fe-bearing phases were well distributed and were removed by pitting without others being exposed. Thus although cathodic currents 100 mV below the pitting potential were initially substantial ( $\sim 45 \mu\text{A}/\text{cm}^2$ ) for 5052 they soon fell to  $1 \mu\text{A}/\text{cm}^2$ . The processed matrix without fibers also performed well in these tests. This work indicated that some corrosion problems associated with solidification microstructures may be exaggerated in composites. It is to be noted that this work was a basic study of corrosion versus microstructure which employed material from the early stages of a processing research program aimed primarily at wetting and bonding questions, and the results do not represent an evaluation of the

potential of the type of processing used.

## 2. Corrosion of an Al-Li/ $\text{Al}_2\text{O}_3$ composite

A brief examination was made with the same procedures as above of a composite with a 35 vol. pct. of the same  $\text{Al}_2\text{O}_3$  fibers in a matrix of commercial purity with nominally 2% Li. The material is prepared by DuPont using an infiltration process, and samples were obtained from R.G. Barrows of NASA Lewis Laboratory. There were distributed pits plus a tendency for some attack in the interface layer region (in this composite this layer is up to a few microns thick and of a complex structure not fully identified). The cathode currents after 24 hours remained many times those of the wrought 5052 and 6061 reference alloys. Microprobe examination could not show the distribution of Li, but did show that there was no strong segregation of the Fe and Si impurities near fibers. The relations between corrosion and microstructure in this material could not be determined by the observations we were able to make.

## 3. Corrosion versus phase distribution in the Al- $\text{Al}_3\text{Fe}$ eutectic alloy

This eutectic with 1.9%Fe (3.5 vol. pct.  $\text{Al}_3\text{Fe}$ ) was chosen as a model system for study of corrosion versus spacing and continuity of a cathodic reinforcing phase at constant volume fraction in a composite with no interface phase. Continuous structures with spacings from 242  $\mu\text{m}$  to 8.6  $\mu\text{m}$  were prepared by directional solidification and one discontinuous eutectic was processed to a mean intercept spacing of 21  $\mu\text{m}$ . There were certain experimental limitations in the need to use small section sizes and in the inability to obtain finer spacings (because a different Al-Fe phase forms at high growth rates). The composites were exposed in free corrosion with periodic cathode polarization. Some hydrogen volumetric measurements, weight loss and anode polarization observations of individual phases were also made.

In one set of experiments, preferential pitting of the matrix was obtained through the choice of a solution containing 5M NaCl at pH 1 in which the  $\text{Al}_3\text{Fe}$  was noncorroding at the pitting potential of the matrix. As more cathode was exposed by pitting, the corrosion rate increased with time at a rate dependent on structure. Equations for corrosion-time were formulated for continuous and discontinuous structures in terms of the parameters of quantitative metallography (such as  $\text{Al}_3\text{Fe}$  surface area per unit volume of composite) derivable from the mean intercept spacing. The model was based on the idealization of random pit nucleation at  $t=0$  and isotropic pit growth. Although pit nucleation and growth were not random in these composites and the equations derived did not give quantitative fits to the data, the data provided support for the basic validity of the idealized models. These models are of value for conceptualizing the effects of microstructure parameters on corrosion. In the continuous case, the predicted corrosion rate is exponential in time and is highly sensitive to intercept spacing. Thus after a certain time a continuous structure with 5  $\mu\text{m}$  spacing could have a corrosion rate at least two orders of magnitude higher than those of 20  $\mu\text{m}$  and coarser spacings, and the exposure time before the onset of rapid corrosion would be longer the larger the

spacing. In our fine continuous structures, the increase of corrosion rate with time was mitigated by breakage of the fine fibers protruding from the pit surface, but it is clear that a too fine continuous structure is undesirable if the reinforcing phase is an effective cathode. In the discontinuous case, the cathodic particles are lost from the pit volume and the increase in corrosion rate was slower with an apparent upper limit. In our discontinuous material, corrosion rate initially increased as  $t^1$  (in the idealized model, the power of  $t$  would appear somewhat higher). Overall, the corrosion rate is predicted to be much less sensitive to decrease of spacing in the discontinuous case.

A second set of experiments was run in 2.4M  $H_2SO_4$ , which gave preferential corrosion of the  $Al_3Fe$  phase, which remained the only significant cathode. In a continuous structure, this could give deep shafts of corrosion. In this situation, the  $Al_3Fe$  (cathode and anode) area was constant but the area of the aluminum matrix, which was a second anode, increased greatly in the walls of the corroded shaft so that corrosion potential fell and with it the corrosion rate of the  $Al_3Fe$ . Under these conditions, fine continuous structures would be preferable to coarse ones. Discontinuous structures approached a steady state in which corrosion of exposed  $Al_3Fe$  particles was balanced by exposure of new ones through slow corrosion of the matrix and were, as expected, superior to continuous ones.

#### 4. Related Projects

Two studies were related to work of Dr. A. Munitz in collaboration with Professor R. Mehrabian's group on processing of composites supported by Grant DAAG-29-78-G-0067.

A. Professor Mehrabian's group had previously made extended studies of the preparation and structure of  $Al/Al_2O_3$  composites, but had not determined the interface phases responsible for bonding. Work was done on composites with Al-Mg matrixes, and Auger and electron diffraction evidence was obtained indicating that a thin  $MgAl_2O_4$  spinel phase was present at the interface.

B. Some questions which arose about the compositions of certain microconstituents in 2024 alloy pointed up the scarcity of information on the insoluble microconstituents in commercial aluminum alloys and the inadequacies of current analytical techniques for small particles. With the aid of Dr. A. Zangvil, who was supported by DOE, a brief investigation of analytical problems was made involving microprobe and analytical electron microscopy, and the need for further development and application of the latter emphasized.

The following relate to electronmicroscopic studies of breakdown and repair of anodic films on aluminum previously sponsored by the U.S. Army Research Office. C and D represent projects conceived and begun under the earlier sponsorship but completed during the present period with principal support from other agencies.

C. Our previous finding, that on forming anodic films on aluminum in sulfuric acid there is film breakdown and transient pitting ("micropitting") even in the absence of chloride, was extended to films formed at a potential substantially lower than in previous work (also supported by DOE).

D. In two-phase Al-Fe alloys anodized in sulfuric acid, three different views had been given in the literature as to the behavior of the  $\text{Al}_3\text{Fe}$  particles. It was demonstrated that these particles do not corrode out but are removed by an excavation process due to preferential transient pitting of the matrix at their margins (also supported by U.S.-Israel Binational Science Foundation and DOE). That  $\text{Al}_3\text{Fe}$  is passive in sulfuric acid at sufficiently high potentials was later demonstrated directly by polarization measurements in the course of our corrosion study of the Al- $\text{Al}_3\text{Fe}$  eutectic (No. 3 above). The sulfuric acid corrosion studies of this eutectic involved potentials in the active-dissolution range of this phase.

E. A review paper was prepared for the Fourth International Symposium on Passivity in October 1977 outlining our work in this field and the insights it may provide on mechanisms of pit initiation, intergranular corrosion and second phase particle behavior.

#### MANUSCRIPTS

"Relation Between Pitting and Structure in Experimental Al-Mg/ $\text{Al}_2\text{O}_3$  Composites" J-Y. Yang and M. Metzger, submitted to Corrosion.

"Some Observations of the Corrosion Behavior of an Al-Li/ $\text{Al}_2\text{O}_3$  Composite" J-Y. Yang and M. Metzger, in preparation.

Effect of Microstructure on the Behavior of Al-Fe Eutectic Alloys During Corrosion of the Cathodic Phase" N.S. Berke and M. Metzger, in preparation.

"Effect of Microstructure on Pitting of the Al- $\text{Al}_3\text{Fe}$  Eutectic Alloy" N.S. Berke and M. Metzger, in preparation.

#### Related Projects

"The Interface Phase in Al-Mg/ $\text{Al}_2\text{O}_3$  Composites" A. Munitz, M. Metzger and R. Mehrabian, Met. Trans. 10A, 1491 (1979)

\*"Analytical Studies on Some Microconstituents in 2024 Aluminum Alloy" A. Munitz, A. Zangvil and M. Metzger, submitted to Met. Trans.

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Princeton, 1978, p. 960.

#### PARTICIPATING PERSONNEL

M. Metzger (Principal Investigator)  
N.S. Berke (Research Assistant)  
A. Munitz (Research Associate,  $\frac{1}{2}$  time)  
J-Y. Yang (Research Assistant)

#### DEGREES AWARDED

N.S. Berke, PhD., June 1980  
J-Y. Yang, MS August, 1980

\*Also received support from other agencies.

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